Hg Substitution Effect on Superconductivity and Crystal Structure of MgB₂

Ya-Jing Cui, Yong-Liang Chen, Ye Yang, Yong Zhang, Cui-Hua Cheng, and Yong Zhao

Abstract—Polycrystalline Mg_{1-x}Hg_xB₂ samples with x=0, 1%, 2.5%, 5%, 7.5%, and 10% have been synthesized by solid-state reaction. Different from the substitution effect of Al, C, Li, etc. on crystal structure of MgB₂, Hg substitution for Mg results in an increase of the lattice constant in both a and c directions. The superconductivity of MgB₂ is also suppressed by Hg substitution. The observed suppression of superconductivity by Hg substitution is discussed in terms of the interband impurity scattering effect in two-band superconductors.

Index Terms—Crystal structure, mercury doping, MgB₂, superconductivity.

1. Introduction

The discovery of the MgB₂ superconductivity has aroused great interest in the field of applied superconductivity because MgB₂ has a critical transition temperature Tc of 39 K[1], reaching the highest Tc in non-cuprate superconductors. Recently, the effect of chemical substitution for Mg or B site has been a subject of interests to understand the characteristic properties of MgB₂, such as the role of multiband in superconductivity mechanisms[2,3]. Among many reports on this subject, the effects of Al substitution for Mg sites[4] and C substitution for B sites[5] have been intensively studied. In addition, other elements, such as Ag[6], Mn[7], Pb[8], Li[9], Ti[10], etc. have also been used as substituents for MgB₂ system, and their substitution effects on the crystal and electronic structures of MgB₂ have been studied.

Although many elements have been investigated as chemical substituents for MgB₂, no research has been reported on the substitution effect of Hg in this system. Since Pb can be doped into MgB₂ and Hg²⁺ has a radius close to that of Pb²⁺, it is quite possible that Hg may be a potential substituent for Mg in MgB₂, thus an alloy like Mg₁₋ₓHgₓB₂ may be formed. In this paper, we report the successful syntheses of polycrystalline Mg₁₋ₓHgₓB₂ alloys as well as the substitution effects of Hg on the structure and superconductivity of MgB₂. Our results show that the superconductivity of MgB₂ is suppressed by partial substitution of Hg for Mg, although Hg substitution results in an increase of the lattice constant.

2. Experimental Details

Mg₁₋ₓHgₓB₂ samples with x=0, 1%, 2.5%, 5%, 7.5%, and 10% were prepared by the solid-state reaction using fine powders of Mg, B and HgO of high purity (≥99.9%). Mixed powders of the raw materials Mg, B and HgO with the stoichiometric ratio of Mg₁₋ₓHgₓB₂ were well mixed in argon atmosphere for 1 h and pressed into pallets. Each pallet was placed and sealed in a quart tube, then sintered at 850 °C for 1 h and cooled to room temperature within the furnace. Because the presence of oxygen in HgO would lead to form MgO in HgO-doped MgB₂, a proper excess amount of Mg was added to compensate the loss of Mg. In this study, HgO rather than pure mercury was chosen as the source of Hg substituent because pure mercury is a liquid at room temperature and very hard to be mixed with other powders.

Powder X-ray diffraction (XRD) was carried out by a Philips X’Pert MRD diffractometer with CuK radiation. Lattice parameters of the samples were obtained from Rietveld refinements of the XRD data. DC magnetization was measured with a Quantum Design MPMS SQUID magnetometer. The Tc was defined as the onset transition in the M(T) curve measured in an applied magnetic field of 20 Oe.

3. Results and Discussion

Fig. 1 shows the XRD patterns for the Mg₁₋ₓHgₓB₂ samples with various Hg contents. MgB₂ is found to be the
main phase in all of these samples. In addition, MgO is observed as impurity phase in most of the samples. The amount of MgO is increasing with the content of HgO. Since the effect of the oxygen is to form MgO in Mg-B-O system, rather than to work as a substituent in MgB$_2$, it is reasonable to believe that the formation of MgO in the present system may be largely attributed to the oxygen in HgO although the oxygen contamination also exists in the processing of the MgB$_2$. Besides, for the samples of high doping level of HgO, MgB$_7$ was detected as another impurity phase, however, its quantity was very small.

Fig. 1. The XRD patterns for Mg$_{1-x}$Hg$_x$B$_2$ samples.

Fig. 2. Enlarged view of the XRD patterns for Mg$_{1-x}$Hg$_x$B$_2$ samples: (a) reflection (100), and (b) reflection (002). The dashed line indicates the original position of the reflection of undoped MgB$_2$.

Besides the existence of some impurity phases, it was also observed that the crystal structure of MgB$_2$ systematically changed with doping level. As shown in Fig. 2 (a) and 2 (b), the positions of the reflections (100) and (002) shift towards lower diffraction angles, indicating an expansion of the lattice constants of MgB$_2$ in both $a$ and $c$ directions. Detailed calculation of the lattice constants obtained from Rietveld refinements revealed that the crystal lattice of MgB$_2$ almost linearly increases with the content of the substituent, as illustrated in Fig. 3. Because the main role of oxygen in HgO is to form MgO, the expansion of the crystal lattice of MgB$_2$ could be attributed to a partial substitution of Hg for Mg. This was also consistent with the fact that both Hg$^{2+}$ and Hg$^{7+}$ had a larger radius than that of Mg$^{2+}$.

Fig. 3. Variation of lattice parameters with doping level for Mg$_{1-x}$Hg$_x$B$_2$ samples.

Fig. 4 shows the temperature dependence of magnetization for Mg$_{1-x}$Hg$_x$B$_2$ samples with various Hg doping levels. All these samples exhibited a superconducting transition above 30 K. The detailed superconducting transition is shown in the inset of Fig. 4, which revealed that the superconductivity of MgB$_2$ was suppressed gradually by Hg substitution for Mg. The depression rate of $T_c$ was around 0.3 K/at%. This rate was smaller than the suppression rates of $T_c$ caused by C substitution for B[8], Al for Mg[5], and Ag for Mg[9], respectively; but larger than the rate caused by Li substitution for Mg[12].

Fig. 4. Temperature dependence of dc magnetization measured in an applied field of 20 Oe for Mg$_{1-x}$Hg$_x$B$_2$ samples. In set: enlarged view for the details of superconducting transition.
Up to now, as reported by many groups\cite{4,13}, the chemical substituent in MgB$_2$, such as Al, C, Ag, Li, etc. always causes a suppression of superconductivity no matter B or Mg is partially substituted. MgB$_2$ is a two-gap superconductor with the existence of two separate sheets of the Fermi surface, one quasi 2D (σ band) and the other quasi 3D (π band)\cite{14,15}. Without any interband coupling or interband scattering of electrons, there would be two transition temperatures. In the case of weak, but finite, interband phonon scattering, the lower $T_c$ disappears and the temperature dependence of the lower gap becomes strongly non-BCS. This leads to a high critical temperature of 39 K and the temperature and field dependent anisotropy of MgB$_2$. Carbon substitution for boron influences mostly intraband scattering in the 2D σ band, and aluminum substitution for magnesium influences mostly intraband scattering in a 3D π band. In both of the cases, additional electrons are introduced in the structure, leading to a hole-filling effect and a decrease of $T_c$. Carbon substitution for boron influences mostly intraband scattering in the 2D σ band, and aluminum substitution for magnesium influences mostly intraband scattering in a 3D π band. In both of the cases, additional electrons are introduced in the structure, leading to a hole-filling effect and a decrease of $T_c$. Carbon substitution for boron influences mostly intraband scattering in the 2D σ band, and aluminum substitution for magnesium influences mostly intraband scattering in a 3D π band. In both of the cases, additional electrons are introduced in the structure, leading to a hole-filling effect and a decrease of $T_c$.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig5.png}
\caption{Variation of $T_c$ with doping level for MgB$_2$ doped with various elements.}
\end{figure}

Different from the hole-filling effect of C and Al, Li doping at Mg site introduces holes into the system, however, the superconducting transition temperature $T_c$ is also decreased. This result together with those of C substitution and Al substitution suggest that MgB$_2$ is optimally doped in nature since both electron doping and hole-doping suppress $T_c$ of the system. Another possible explanation for the suppression of $T_c$ by these substituents may be the “chemical pressure” effect because these substituents also cause a decrease of the lattice parameters while suppressing the superconductivity, which is similar to the hydrostatic pressure effect on MgB$_2$\cite{15}.

However, for the present system, Hg substituting for Mg does not induce hole filling effect because valence state of Hg is only Hg$^2+$ and Hg$^{2+}$. Hg substituting for Mg also does not induce “chemical pressure” because the lattice constant does not decrease with Hg doping. The suppression of superconductivity by Hg substitution may be attributed to the modification of the interband coupling because Hg substitution for Mg lengthens the distance between the boron sheets and introduces impurity scattering of electrons in the 3D π band. Recent calculation shows\cite{17} that the modification of the interband coupling may cause a significant decrease of $T_c$ in two-band BCS-superconducting system, such as MgB$_2$. Under the assumption that the off-diagonal elements are small as compared with the diagonal ones, i.e., $\lambda_{12}, \lambda'_{31}\ll\lambda'_{11}=\lambda'_{22}, \lambda'_{23}$, (here $\lambda'_{ij}$ is the elements in the matrix of the effective electron-phonon coupling integral), which means the interband electron-phonon coupling is much weaker than the intraband coupling, the effect of impurities on $T_c$, the change $\Delta T_c=T_{c0}-T_c$ for small impurity scattering can be written in

$$\Delta T_c/T_{c0} \approx 7 \tau_{12}(1+\lambda'_{11}+\lambda'_{12})$$

where $T_{c0}$ and $T_c$ are superconducting transition temperatures without and with impurity scattering, respectively, $\tau_{12}$ is the nonmagnetic impurity scattering rate, $\lambda'_{11}$ and $\lambda'_{12}$ correspond to the intraband (band 1) and interband electron-phonon coupling constants, respectively. Equation (1) suggests that the superconductivity is suppressed with increasing interband impurity scattering (i.e., increasing $\tau_{12}$) or weakening the interband electron-phonon coupling (i.e., decreasing $\lambda'_{11}$ or $\lambda'_{12}$ or both of them). In our experiments, increasing the impurity (i.e., Hg) content corresponds to the increase of impurity scattering rate, $\tau_{12}$; and the consequent increase of distance between the boron sheets may result in the weakening of the interband electron-phonon coupling $\lambda_{12}$. According to (1), both of these effects will decrease the superconducting transition temperature of two-band BCS-superconducting system with interband impurity scattering.

In addition, it should be pointed that the observed changes of $T_c$ and the lattice constants in the present system cannot be attributed to the lack of magnesium although MgO forms as impurities in the samples. This is because that a proper extra amount of Mg has been already added in the raw materials to compensate the loss of Mg by forming MgB$_2$. On the other hand, Mg vacancy usually results in a contraction of the MgB$_2$ lattice in a direction\cite{18}. The depression rate of $T_c$ caused by Mg vacancies is much smaller than the observed one in Hg substituted in MgB$_2$ compared in Fig. 5. Oxygen incorporation may be another cause for the suppression of superconductivity in MgB$_2$\cite{19,20}. However, this happens usually when the samples (mainly thin films) were prepared in an oxygen rich atmosphere and at a relatively low reaction temperature (e.g. 500 C to 670 C) for a short reaction time (e.g. 20 min). If excess Mg presents during the growth of MgB$_2$, oxygen incorporation can be largely reduced by forming MgO precipitates\cite{21}. Due to the reason, excess amount of Mg has been added to prevent the oxygen incorporation in MgB$_2$ in the present study. Therefore, oxygen incorporation should
not be the main reason for the $T_c$ depression observed in our experiments. The presence of MgO impurity phase in the HgO doped MgB$_2$ is another possible source for the $T_c$ suppression as reported by Jiang $et$ $al.$[22]. However, the suppression rate of $T_c$ by MgO is around 0.10 K/at%, which is significantly smaller than the observed suppression rate of 0.3K/at% in our study, thus cannot be the dominant factor for the $T_c$ suppression observed in HgO doped MgB$_2$. Taking away the contribution of MgO to the $T_c$ suppression, the net suppression rate by Hg doping can be estimated to be 0.2 K/at%.

4. Conclusions

In summary, we have successfully synthesized Mg$_{1-x}$Hg$_x$B$_2$ alloys with $x=0$, 1%, 2.5%, 5%, 7.5%, and 10%. It is observed that Hg substitution increases the lattice constants of MgB$_2$ in both $a$ and $c$ directions, which is quite different from the substitution effects of Al, C, Li, etc. on the crystal structure of MgB$_2$. As a result of Hg substitution, the superconductivity of MgB$_2$ is suppressed. The suppression of superconductivity of MgB$_2$ by Hg substitution may be due to the interband impurity scattering effect which modifies the interband coupling and consequently decreases the $T_c$ of this two-band superconducting system.

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References


Ya-Jing Cui was born in Hebei Province, China, in 1982. She received the B.S. degree in material science and engineering from Southwest Jiaotong University (SWJTU), Chengdu, in 2004. She is currently pursuing the Ph.D. degree together with M.S. degree with the Superconductivity R&D Center (SRDC), SWJTU. Her research interests include new materials in superconductors.

Yong-Liang Chen was born in Shanxi Province, China, in 1979. He received the B.S. degree from College of Physics and Electronics of Shanxi University (SXU), Taiyuan, in 2003. He is currently pursuing the Ph.D. degree together with M.S. degree with SRDC, SWJTU. His research interest is in superconducting materials.

Ye Yang was born in Zhejiang Province, China, in 1981. He is a researching trainee in SRDC, SWJTU, Chengdu. He received the M.S. degree in electric engineering and automation from SWJTU, Chengdu, in 2004. He is currently pursuing the Ph.D. degree with SRDC, SWJTU. His research interests include materials, physics and applications of superconductors.

Yong Zhang was born in Sichuan, China, in 1969. She received the M.S. degree of Physical Chemistry from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences (CAS), in 1994. She is associate professor in SRDC, SWJTU. She is currently pursuing the Ph.D. degree at SWJTU. Her research interests include the processing and applications of superconducting materials.

Cui-Hua Cheng was born in Wuhan, China, in 1960. She received the Ph.D. degree in materials science from School of Materials Science and Engineering at the University New South Wales, Australia, in 2002. She is currently a research fellow with the University of New South Wales, Australia. Her research interests include the processing and physical properties of superconducting and magnetic materials.

Yong Zhao was born in Wuhan, China, in 1960. He received the Ph.D. degree in condensed matter physics from the University of Science and Technology of China, in 1988. He has engaged in the superconductivity research since 1985. He is currently a professorial research fellow with the University of New South Wales, Australia, and also the leader for superconductivity research in the Southwest Jiaotong University. His research interests mainly include the processing and physical properties of superconducting and magnetic materials.